picrate, yellow prisms, m.p. 128~129° (EtOH). *Anal.* Calcd. for $C_{18}H_{22}O_7N_4$: C, 53.20; H, 5.42; N, 13.79. Found : C, 53.14; H, 5.63; N, 13.96.

In order to demonstrate the α,β-enamine structure in the VI, to a solution of the perchlorate (VII) was added conc. potassium cyanide solution dropwise with stirring. In this case the cyano-compound (VIII) was also obtained in a quantitative yield : b.p$_3$ 135~138° (oil bath temp.), IR $\lambda_{\max}^{\text{Liquid}}$ cm^{-1} : 2730, 2807 (*trans*-quinolizidine), 2250 (CN) and no band near 1652 due to $(\rangle C=\overset{|}{C}-N\langle)$.

Attempted recrystallization of the picrate of VIII from hot ethanol yielded instead the picrate of VI by elimination of hydrocyanic acid.

The dehydrogeneration of VI to pyrido[2,1,6-de]quinolizine is now in progress.

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Shihunine : A New Phthalide-Pyrrolidine Alkaloid

A Chinese drug known in Japanese as "Chukanso" (中環草) is sometimes available on the Hong Kong market as a kind of Shih-Hu (Japanese name "Sekkoku") and is derived from the orchidaceous plant, *Dendrobium lohohense* Tang et Wang.[*1,1)]

We have isolated a crystalline alkaloid from Chukanso, shihunine, m.p. 79°, pKa 3.65,[*2] *Anal.* Calcd. for $C_{12}H_{13}O_2N$: C, 70.91; H, 6.45; N, 6.89., mol. wt., 203.23. Found: C, 70.53; H, 6.54; N, 6.59., mol. wt.,[*3] 200, 209. It formed a picrate, m.p. 163~164°, *Anal.* Calcd. for $C_{12}H_{13}O_2N\cdot C_6H_3O_7N_3$: C, 50.00; H, 3.73; N, 12.96. Found : C, 50.18; H, 3.78; N, 12.74.

Shihunine is racemic ($[\alpha]_{200\sim700\,m\mu}$ 0°) and has a lactone grouping (IR $\nu_{\max}^{CCl_4}$ cm^{-1} : 1761; $\nu_{\max}^{\text{Nujol}}$ cm^{-1} : 1743). On permanganate oxidation it yielded phthalic acid identified by comparison of its infrared spectrum with that of authentic sample and by melting point of its anhydride, and mixed m.p. 132~134°.

Shihunine when stirred with Adams catalyst in hydrogen took up one mole of hydrogen and furnished an amino acid, m.p. ca 200°, IR $\nu_{COO^-}^{\text{Nujol}}$ cm^{-1} : 1613, pKa 3.3, 10.5, *Anal.* Calcd. for $C_{12}H_{15}O_2N$: C, 70.22; H, 7.37; N, 6.82. Found : C, 69.99; H, 7.45; N, 7.00. It formed a picrate, m.p. 155~156°, IR $\nu_{COOH}^{\text{Nujol}}$ cm^{-1} : 1684, *Anal.* Calcd. for $C_{12}H_{15}O_2N\cdot C_6H_3O_7N_3$: C, 49.77; H, 4.18; N, 12.90. Found : C, 49.92; H, 4.09; N, 13.09. The

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[*1] The botanical origin of this drug was authenticated by Dr. S. Takahashi of this Faculty to whom the authors are indebted.

[*2] Melting points were measured on a Kofler hot-stage and are given as uncorrected values, and pKa were measured in 50% EtOH-H$_2$O.

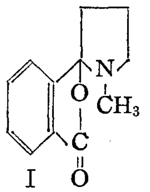
[*3] The molecular weight was measured by Rast's method.

1) Zhung-jau-zhi (中葯志), **111**, pp. 39 (1961); T. Tang, F. Wang : Acta Phytotaxonomica, **1**, 82 (1951).

amino acid on dry distillation with barium oxide was smoothly decarboxylated to yield an oily amine, pKa 8.2 (picrate, m.p. 150~153°, *Anal.* Calcd. for $C_{11}H_{15}N \cdot C_6H_3O_7N_3$: C, 52.30; H, 4.65; N, 14.35. Found : C, 52.60; H, 4.61; N, 14.44, methiodide, m.p. 157~159°, *Anal.* Calcd. for $C_{12}H_{18}NI$: C, 47.52; H, 5.94; N, 4.62. Found : C, 47.80; H, 5.88; N, 4.74) which was identical with an authentic specimen of 1-methyl-2-phenylpyrrolidine[2] (Ⅲ) (as shown by the mixed melting point and comparison of the infrared spectra of the picrates).

Lithium aluminum hydride reduction of shihunine was accompanied by hydrogenolysis and yielded a mono-ol, oil, pKa 8.34 (picrate, m.p. 128~130°, *Anal.* Calcd. for $C_{12}H_{17}ON \cdot C_6H_3O_7N_3$: C, 51.42; H, 4,80; N, 13.33. Found : C, 51.15; H, 4.86; N, 13.23). The same mono-ol was also produced by lithium aluminum hydride reduction of the amino acid, which could easily be acetylated by acetic anhydride and pyridine to an acetate, oil, IR $\nu_{\max}^{\text{film}}$ cm^{-1} : 1740 (OAc), pKa 7.8 (picrate, m.p. 174~176° (decomp.), IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1} : 1736 (OAc), *Anal.* Calcd. for $C_{14}H_{19}O_2N \cdot C_6H_3O_7N_3$: C, 51.95, H, 4.80; N, 12.12. Found : C, 52.18; H, 4.80; N, 11.94). The nuclear magnetic resonance spectrum of the acetate showed a sharp singlet peak at δ 5.19 corresponding to two hydrogens which was obviously attributable to the C_6H_5-CH_2-OAc grouping. Hence the amino acid should be represented by the structure (Ⅱ).

The structure of shihunine can be deduced by comparison of the marked difference in basicities (4.6~4.7) of shihunine and the mono-ol and the amine (Ⅲ), which showed that the original molecule must contain the -CO-O-C-N- grouping. This structure (I) agrees well with the hydrogenolyzable nature of shihunine. Hence shihunine must be represented by structure (I). An alternative structure was excluded by the fact that the nuclear magnetic resonance spectrum of shihunine did not exhibit any proton attributable to a -CO-O-C$\underline{H}$-N- grouping, but cleary showed three well separated complex peaks centered at δ 7.7 (aromatic protons), 3.2 (-N-CH_2-) and 2.3 (-CH_2-CH_2-) in the ratio of 4:2:4 and also a sharp singlet at δ 2.10 (3H) due to a N-methyl grouping.



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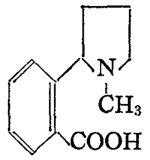
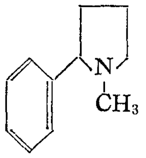


Ⅱ



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[2] J.H. Burckhalter, J.H. Short : J. Org. Chem., **23**, 1281 (1958).